METHOD OF DESULPHONATING DIAMINODIPHENYLAMINE-2-SULPHONIC ACID COMPOUNDS

Luther M. Lauer, Orchard Park, N. Y., assignor
to National Aniline & Chemical Company, Inc.,
New York, N. Y., a corporation of New York

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This invention relates to an improved method of preparing diaminodiphenylamine compounds. It relates more particularly to the manufacture of 4,4'-diaminodiphenylamine from 4,4'-diamino-
diphenylamine-2-sulphonic acid.

It has hitherto been customary to prepare 4,4'-
diaminodiphenylamine in accordance with two
general methods: the first of these comprises the
oxidation of a mixture of aniline and para-
phenylene diamine to form indamine which is
subsequently reduced to the desired product; and
the second, which is the method used most gen-
erally for commercial purposes, comprises the
reduction of 4,4'-dinitro or 4-nitro-4'-aminodiphenylamine or salts thereof in aqueous medium,
the nitro groups being reduced to amino groups.

However, because both the intermediates and
the products are insoluble in water these reduc-
tion processes are characterized by low yields
and by long and troublesome manipulations.
During such reduction processes, side reactions
occur which result in the production of consider-
able quantities of organic by-products of an
insoluble nature, and these, together with large
amounts of metal oxides or other inorganic sludges
which result from the reducing agents used, precipitate and become intermingled with the re-
quired amino compounds. As a result specific methods, which are quite tedious and costly, must
be employed in order to isolate pure 4,4'-diamino-
diphenylamine from the impurities associated therewith.

It is the object of the present invention to OVERCOME THE DISADVANTAGES OF THE PRIOR PROCESSES by providing a method for the preparation of a diaminodiphenylamine compound by the
desulphonation of a diaminodiphenylamine sul-
phonic acid compound of the type to be herein-
after described.

I have found that the desulphonation of di-
aminodiphenylamine sulphonic acid compounds
which, in the form of the free sulphonic acids, correspond with the general structural formula:

\[
\text{HN-SO}_2H \quad X \quad 
\]

Can be effected by subjecting said compounds to
hydrolysis with the aid of a non-oxidizing min-
eral acid, preferably under the conditions of
temperature and concentration which are more
fully described hereinafter. In this formula X
represents a hydrogen atom, an alkyl group (f. i.,
CH₃, C₂H₅, C₃H₇, etc.), an alkoxy group (f. i.,
OCH₃, OCH₂H, O₂CH₂H, etc.) or a halogen atom
(f. i., Cl or Br), Y represents a hydrogen atom
or an alkyl group (f. i., one of the foregoing)
and Z represents a hydrogen atom or an alkyl
group which may be the same as that represented
by Y or different.

In carrying out the process of this invention I
proceed in accordance with the following ex-
ample, it being understood, however, that it is
not intended to limit the scope of the invention
thereto.

Example:—277 parts by weight of 4,4'-di-
aminodiphenylamine-2-sulphonic acid are sus-

cended in about 1110 parts by weight of about
75% sulphuric acid. The yellow slurry which is
thus formed is heated, with constant agitation,
to a temperature of about 100° to about 110° C.
and held at this temperature for about 1½ hours or
until the desulphonation is complete. At the
completion of the desulphonation, the slurry is
20 diluted with water, cooled to a temperature of
about 20° C. to about 30° C. and filtered. The
filtrate is discarded and the residue is washed with
cold water until the water becomes faintly acid
after passing through the residue. The washed
55 faintly acid precipitate is then suspended in cold
water and the aqueous slurry is vigorously agi-
tated. A dilute solution of soda ash or similar
alkali is then added to this agitated slurry until
it is faintly alkaline. The alkaline mass is filter-
ed, the filtrate discarded, and the residue which
consists of precipitated 4,4'-diaminodiphenyl-
amine is washed with cold water until the water
passing through the residue is quite free of alkali.
The washed precipitate is then dried in a suitable
manner.

In order to determine when the desulphonation
reaction above described is completed, a few drops
of the slurry are diluted with about 20 cc. of hot
water and the mixture is made slightly alkaline
with ammonia. The solution is filtered, cooled
and made acid with dilute sulphuric or hydro-
chloric acid. The presence of any diaminodih-
phenylamine-2-sulphonic acid in the sample is
evidenced by the formation of a precipitate. Complete desulphonation is indicated by the
absence of any precipitate, or by the formation of
an extremely small quantity of precipitate.

It will be understood that this invention is
not limited to the details given in the above
example but that changes may be made without
departing from the scope thereof.

Thus, aqueous sulphuric acid of other con-
centrations may be employed and the temperature
at which the hydrolysis is carried out and its
duration may be varied. These factors are interrelated, a higher temperature and/or a more extended reaction period being employed with a more dilute sulphuric acid. The use of highly concentrated sulphuric acid is not desirable in view of its tendency to cause sulphonation, particularly at the higher temperatures. For example, satisfactory results may be obtained by the utilization of sulphuric acid ranging in concentration from about 60% to about 80% and at temperatures ranging from about 60° to about 130° C.

The hydrolysis may also be carried out with the aid of other non-oxidizing mineral acids, as for example, hydrochloric acid, but the use of sulphuric acid is preferred.

Furthermore, the hereindescribed hydrolysis treatment may be employed for the desulphonation of other diamino-diphenylamine sulphonic acid compounds (i.e., 4,4'-diamino-3'-methyl-diphenylamine-2-sulphonic acid, 4,4'-diamino-3'-chloro-diphenylamine-2-sulphonic acid, 4,4'-diamino-3'-bromo-diphenylamine-2-sulphonic acid, 4,4'-diamino-3'-methoxy-diphenylamine-2-sulphonic acid, 4,4'-diamino-3'-ethoxy-diphenylamine-2-sulphonic acid, 4-amino-4'-methylamino-diphenylamine-2-sulphonic acid, 4-amino-4'-ethylnamino-diphenylamine-2-sulphonic acid, 4-amino-4'-propylamino-diphenylamine-2-sulphonic acid, 4-amino-4'-dimethylamino-diphenylamine-2-sulphonic acid, 4-amino-4'-diethylamino-diphenylamine-2-sulphonic acid, 4-amino-4'-dipropylamino-diphenylamine-2-sulphonic acid, etc.) and salts of the diamino-diphenylamine sulphonic acid compounds, and especially their ammonium and alkali metal salts.

I claim:

1. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid compound which, in the form of the free sulphonic acid, corresponds with the general structural formula

\[
\text{H}_2\text{N}-\text{SO}_2\text{H}-\text{X}-\text{NYZ}
\]

wherein X represents a hydrogen atom, an alkyl group, an alkxy group or a halogen atom, Y represents a hydrogen atom or an alkyl group, and Z represents a hydrogen atom or an alkyl group, which comprises subjecting the same to hydrolysis in the presence of a non-oxidizing mineral acid.

2. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid compound which, in the form of the free sulphonic acid, corresponds with the general structural formula

\[
\text{H}_2\text{N}-\text{SO}_2\text{H}-\text{X}-\text{NH}_3
\]

wherein X represents a hydrogen atom, an alkyl group, an alkxy group or a halogen atom, which comprises treating the same with an aqueous non-oxidizing mineral acid.

3. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid compound corresponding with the general structural formula

\[
\text{H}_2\text{N}-\text{SO}_2\text{M}-\text{X}-\text{NH}_2
\]

wherein X represents a hydrogen atom, an alkyl group, an alkxy group or a halogen atom and M represents hydrogen, ammonium or an alkali metal, which comprises treating the same with an aqueous sulphuric acid.

4. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid compound corresponding with the general structural formula

\[
\text{H}_2\text{N}-\text{SO}_2\text{M}-\text{X}-\text{NH}_2
\]

wherein M represents hydrogen, ammonium or an alkali metal, which comprises subjecting it to hydrolysis in the presence of a non-oxidizing mineral acid.

5. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises heating it with an aqueous non-oxidizing mineral acid.

6. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises heating it with sulphuric acid having a concentration of from about 60 per cent to about 80 per cent.

7. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises heating it with aqueous sulphuric acid at a temperature of from about 60° to about 130° C.

8. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises heating it at a temperature of from about 60° to about 130° C. With a solution of sulphuric acid having a concentration of from about 60 per cent to about 80 per cent.

9. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises heating it at a temperature of from about 100° to about 110° C. With a solution of sulphuric acid having a concentration of from about 60 per cent to about 80 per cent.

10. A method for the desulphonation of a 4,4'-diamino-diphenylamine-2-sulphonic acid which comprises treating said compound at a temperature of from about 100° C. to about 110° C. With a solution of sulphuric acid having a concentration of about 76 per cent.

LUTHER M. LAUER.